

# Adsorption characteristics of thorium on silica-based anion exchange resins\*

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To isolate and separate thorium from nitric acid solutions, three silica-based anion exchange resins were synthesized. Batch experiments were carried out to investigate adsorption behavior of thorium in nitric acid solutions. Adsorption at different concentrations of nitric acid and thorium, influence of contact time and coexisting metal ions, and effect of  $\text{NO}_3^-$  were investigated in detail. It was found that at high  $\text{HNO}_3$  concentrations, the resins exhibited higher adsorption capacity and better affinity towards thorium. The adsorption kinetics could be described by the pseudo-second order model equation, while the adsorption isotherms were well correlated by the Langmuir model. The maximum capacity towards thorium species on SiPyR-N4 was evaluated at 27–28 mg/g-resin. The thermodynamic parameters indicated the adsorption was an exothermic reaction. The presence of  $\text{NO}_3^-$  was found to promote the retention of the thorium species.

Keywords: Thorium, Silica, Anion exchange resin, Adsorption

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## I. INTRODUCTION

Almost all the nuclear reactors are based on the use of uranium with very little recycling of the fuel. This is not a sustainable mode of the world with increasing demand of energy for development. As thorium is 3–4 times more abundant than uranium [1], much attention has been paid on use of thorium in the CANDU, LWRs, and molten salt reactors [2–4]. It is believed that thorium fuel cycle has the main advantage of smaller initial inventory and reduced radioactive wastes formation [5]. In this context, India has been developing the technology based on thorium cycle after detention of limited uranium amounts and large deposits of thorium [6]. However, to use thorium as a nuclear fuel, we need to find a method to reprocess thorium fuel.

Similar to UREX and PUREX process, a method based on extraction of thorium and uranium by tri-n-butyl phosphate (TBP), namely THOREX, was developed in the thorium fuel cycle [7]. It has some disadvantages such as large amounts of waste formation and large scale extraction equipment [8], hence the need of an advanced fuel cycle process with compact equipment and less radioactive waste for efficient use of Th-based fuels.

Ion exchange has been applied to reprocess spent nuclear fuels for over 70 years for its simple operation, organic solvent free feature and compact equipment. Conventional organic ion exchangers are of poor radiation resistance and slow adsorption rates [9, 10], so silica-based ion exchangers were developed, with fast retention kinetics, good radiation resistance and low pressure loss in a packed column. The materi-

als perform better in the recovery of uranium, plutonium and neptunium from spent nuclear fuels [9, 11, 12]. They also reveal great affinity to some specific fission products such as Pd, Ru and Tc [13]. They can be used to adsorb and separate rare earth elements [14, 15]. The silica-based anion exchangers include the weak-base anion exchange resin (SiPyR-N3) [16], strong-base anion exchange resin (SiPyR-N4) [15] and resin with complex functional groups (AR-01) [17]. Structures of the functional groups are shown in Fig. 1.

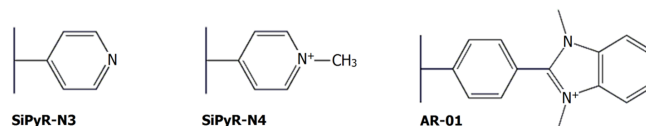


Fig. 1. Structures of functional groups of silica-based anion exchange resins.

Feasibility of adsorbing thorium with anion exchangers in hydrochloric, nitric, and sulfuric acid media was investigated many years ago [18]. Some commercial anion exchangers, such as Dowex-1 and Dowex-2, show good adsorption and separation properties toward thorium [19, 20]. The silica-based anion exchange resins have not been extensively applied yet in the recovery of thorium species. In this paper, we report our study on adsorption behavior of thorium from nitric acid solutions by the use of silica-based anion exchangers for potential full scale applications of thorium fuel cycle in power plants.

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## II. EXPERIMENTAL

### A. Materials

Silica particles of 600 nm mean pore size and 37–74  $\mu\text{m}$  in size were used as base material of the resins. To synthesize the silica-based anion exchangers, two monomers were provided by J&K Scientific Ltd. The DVB (divinyl benzene) was a m- and p-mixture in 55% purity, mixed with EVB (ethyl-vinyl benzene) and DEB (diethyl benzene) and stabilized with TBC (tert-butyl-catechol). The polymerization retarder was washed by sodium hydroxide solution. The 4VP (4-vinylpyridine), purified 95% purity through vacuum distillation, was stabilized with TBC. Acetophenone and diethyl-o-phthalate in analytical reagent purity, from Sinopharm Chemical Reagent Co., Ltd., were used as solvent. AIBN ( $\alpha, \alpha'$ -azobisisobutyronitrile) in chemical pure purity, from Tianjin Guangfu Fine Chemical Research Institute, and ACCN (1,1'-azobiscyclohexane-1-carbonitrile) in 98% purity, from Sigma-Aldrich Co., Ltd, were used as initiators.  $\text{Th}(\text{NO}_3)_4$  was from Aladdin Chemistry Co., Ltd. The other nitrates and  $\text{HNO}_3$ , all of analytical degree, were from Sinopharm Chemical Reagent Co., Ltd. Ruthenium (III) nitrosyl nitrate, a solution containing 1.5wt% Ru in dilute  $\text{HNO}_3$ , was from Sigma-Aldrich Co., Ltd. De-ionized water (18 M $\Omega$ ) was used in the experiments.

### B. Synthesis of the resins

After washed by hydrochloric acid and vacuum-dried, the silica particles were placed in a rotary evaporator flask connected with a vacuum pump. A mixture of monomers (85wt.% 4VP and 15wt.% DVB), initiators (AIBN and ACCN) and diluents (acetophenone and diethyl-o-phthalate) was sucked into the flask, which was rotated slowly so that the silica pores could be filled with the mixture completely. Then, under protection of nitrogen gas, the flask was heated to 363 K gradually in a silicone-oil bath and rotated at 363 K for 20 h for polymerization of the monomers. The synthesized SiPyR-N3 was washed by water and acetone in turn for several times.

To investigate the pore size effect on properties of the resins, the silica particles in mean pore size of 50 nm were also used in synthesis of SiPyR-N3.

To get SiPyR-N4, SiPyR-N3 was converted to quaternary ammonium by reacting with dimethylsulphate. AR-01 was synthesized in similar way.

The synthesized resins were characterized by FTIR analysis (Shimadzu IRAffinity-1 with ATR attachment), TG-DTA analysis on a thermal gravimetry analyzer (Shimadzu T-60) under oxygen atmosphere, with the samples being heated from 30  $^{\circ}\text{C}$  to 550  $^{\circ}\text{C}$  in heating rate of 1  $^{\circ}\text{C}/\text{min}$ , and scanning electron microscopy (Sirion 200). The surface area and pore size were measured by Accelerated Surface Area and Porosimetry System (ASAP 2020). The exchange capacity was determined by titration.

### C. Batch experiments

Batch experiments of thorium adsorption were carried out in a thermostatic air shaker, to study effects of the acidity and initial thorium concentration, the adsorption kinetics, and the retention performance of thorium compared with accompanying metal ions. The resins were prepared for the batch adsorption experiments. They were transferred into  $\text{NO}_3^-$  condition of different concentrations. Each type of the resins was packed into a sand core funnel connected with a dropping funnel. Nitric acid was added into it in drops. Then, the samples were transferred into a sand core funnel to evacuate the solution, vacuum-drying.

The equilibrium adsorption capacity ( $Q_e$ , mmol/g) and distribution coefficient ( $K_d$ ,  $\text{cm}^3/\text{g}$ ) were calculated by:

$$Q_e = (C_0 - C_e)V/(Mm), \quad (1)$$

$$K_d = (C_0 - C_e)V/(C_e m), \quad (2)$$

where,  $C_0$  and  $C_e$  denote the initial and equilibrium concentrations in aqueous phase (mg/L), respectively;  $M$  is the Th molar mass.  $m$  is the mass of resins (g); and  $V$  is the volume of aqueous phase in batch experiments ( $\text{cm}^3$ ).

#### 1. Influence of the concentration of nitric acid

In nuclear fuel reprocessing process, spent fuel is dissolved by nitric acid. In  $\text{HNO}_3$  of different concentrations, the thorium adsorption behavior onto anion exchange resins may change obviously, hence the need of investigating the  $\text{HNO}_3$  concentration effect. In industrial nuclear fuel reprocessing process, the  $\text{HNO}_3$  concentration is 3–6 M. Therefore, the batch experiments were carried out in  $\text{HNO}_3$  solutions of 0.1–9 M.

The initial concentration of thorium was 10 mM and the contact time was 2 h.

#### 2. Adsorption kinetics

To investigate the adsorption kinetics, experiments were performed with a different contact time from 5 min to as long as 2 h, when an equilibrium of thorium adsorption is surely attained. The  $\text{HNO}_3$  concentration was 3 M and the initial thorium concentration was 10 mM.

#### 3. Adsorption isotherm

To investigate thorium adsorption capacity, adsorption isotherms were obtained through the batch experiments in a wide range of initial thorium concentration from 1 mM to as large as 40 mM, where saturation of the Th adsorption should be attained. The  $\text{HNO}_3$  concentration was 3 M and the contact time was 2 h.

#### 4. Influence of nitrates

To understand mechanism of the adsorption, nitrate salts were added into the solutions to investigate the nitrate effect on thorium retention. It has been found that nitrate salts enhance the uptake of uranium onto anion exchange resins with effectiveness in the order as follows:  $\text{Al}(\text{NO}_3)_3 > \text{Ca}(\text{NO}_3)_2 > \text{LiNO}_3 > \text{NH}_4\text{NO}_3 > \text{HNO}_3$  [21]. Also, it has been proved that  $\text{NH}_4\text{NO}_3$  and  $\text{Mg}(\text{NO}_3)_2$  can improve thorium adsorption effectively [21]. Therefore,  $\text{NaNO}_3$  and  $\text{Mg}(\text{NO}_3)_2$  were used to study their influence on thorium adsorption. Considering solubility of the nitrates, the concentration of nitrate salts was limited under 3 M.

The initial thorium concentration was 10 mM and the contact time was 2 h.

#### 5. Adsorption thermodynamics

To investigate temperature effect on the adsorption, batch experiments were conducted at 25 °C, 30 °C, 35 °C, 40 °C and 45 °C, at contact time of 2 h,  $\text{HNO}_3$  concentration of 9 M and initial Th concentration of 10 mM.

#### 6. Separation of thorium from accompanying metals in nitric acid solution

To use the silica-based anion exchange resins in thorium fuel cycle, it is necessary to investigate the possibility of separating thorium from accompanying metal ions in nitric acid solutions, i.e., representative fission products such as ruthenium, palladium, strontium, zirconium, and rare earth metals, which were added into the nitric acid solution for experiment. The  $\text{HNO}_3$  concentration ranged from 0.1 M to 6 M, so as to optimize the thorium separation condition. The initial concentration of metal ions was 10 mM and the contact time was 2 h.

Throughout all the batch experiments, the air shaker was controlled at 298 K, the phase ratio was 0.1 g of resin to 5 mL of solution, and the samples were shaken at a frequency of 120 r/min.

After the adsorption, a phase separation was achieved using membrane filters of 0.45  $\mu\text{m}$  in mean pore size. The concentrations of thorium in the aqueous phase before and after adsorption were determined using ICP-AES spectrometer (Shimadzu ICP-7510).

#### D. Desorption experiment

Under the best condition of thorium adsorption, the resins attained adsorption equilibrium were dried, and the amount of thorium adsorbed onto the resins were calculated from thorium concentrations in the solutions before and after adsorption. The resins and eluent were mixed in the phase ratio of 0.1 g resin to 5 mL eluent, at 298 K and shaking at 120 r/min.

The thorium concentration was detected by ICP-AES and the elution rate was calculated.

### III. RESULTS AND DISCUSSION

#### A. Characterization of the silica-based anion exchange resins

SEM images (Fig. 2) of the SiPyR-N4 resin show obvious porous structure. The results of BET test proved existence of the porous structure, too. SEM images of the SiPyR-N3 (Fig. 3(a)) and AR-01 (Fig. 3(b)) resins show similar porous structure, but the pore size of SiPyR-N3 is much smaller. In the synthesis procedures, SiPyR-N3 was fabricated based on the silica particles in mean pore size of 50 nm, which is much smaller than those of the other resins (i.e., 600 nm) synthesized under the same conditions except that the silica particles are of larger pore size. The results of FTIR, TG-DTA, titration and BET revealed that the resins have similar characteristics to what have been reported previously. Main physical and chemical parameters of the silica-based resins are listed in Table 1 [15–17].

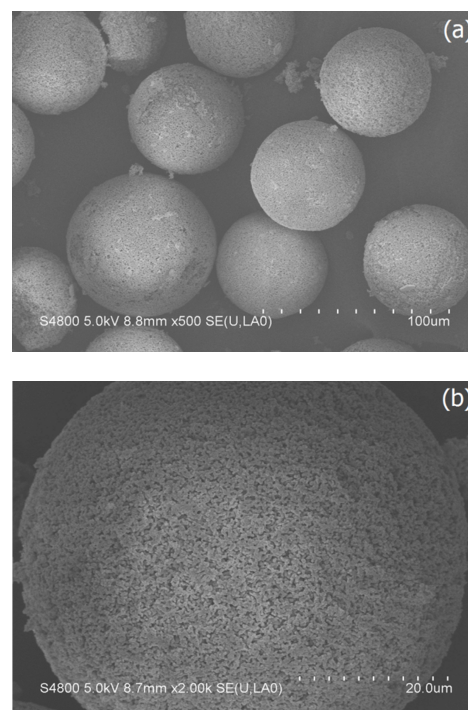


Fig. 2. SEM images of SiPyR-N4 resin. Magnification: (a): 500; (b): 2000.

#### B. Batch adsorption experiment

##### 1. The $\text{HNO}_3$ concentration effect

The hydrolysis of  $\text{Th}^{4+}$  may occur in a low concentration of nitric acid, which would disturb the aimed reaction processes

TABLE 1. Characterization of silica-based anion exchange resins of 37–74 μm in size

Adsorbent	Silica pore size (nm)	Impregnated polymer ratio (wt.%)	Total capacity (meq/g)	Quaternary capacity (meq/g)
SiPyR-N3	50	22.7	4.5	—
SiPyR-N4	600	27	4.5	4.5
AR-01	600	27	4.2	2.1

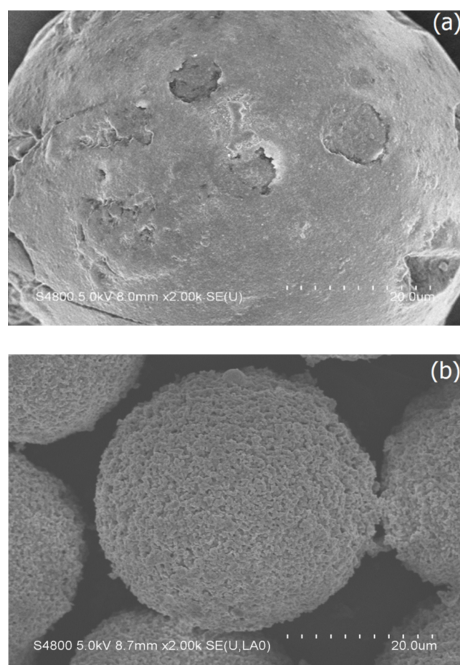
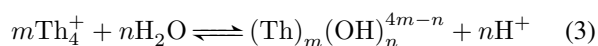
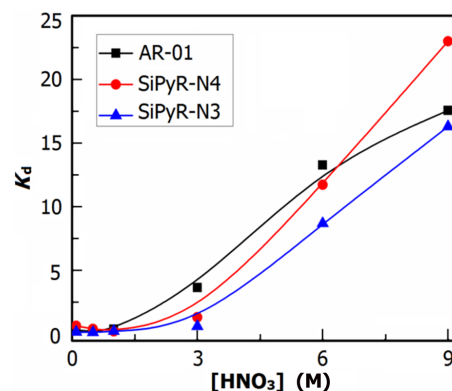


Fig. 3. SEM images of SiPyR-N3 (a) and AR-01 (b). Magnification: 2000.

of adsorption. It was reported that obvious hydrolysis of  $\text{Th}^{4+}$  occurred when the solution is of pH value of higher than 2, as described in Eq. (3) [22]. In this work, the  $\text{HNO}_3$  concentrations were 0.1–9 M and in this situation thorium was supposed to exist as  $\text{Th}^{4+}$  or the  $[\text{Th}(\text{NO}_3)_n]^{4-n}$  ligand complex.



As shown in Fig. 4,  $\text{HNO}_3$  concentration affects strongly the thorium adsorption. At low acidity, the resins adsorb little thorium. In this condition, most thorium ions are cations, such as  $\text{Th}^{4+}$ ,  $[\text{Th}(\text{NO}_3)]^{3+}$ ,  $[\text{Th}(\text{NO}_3)_2]^{2+}$  and  $[\text{Th}(\text{NO}_3)_3]^+$ , which have no affinity to anion exchange resins. With increasing concentration of  $\text{NO}_3^-$ , thorium ions get more ligands and form  $[\text{Th}(\text{NO}_3)_5]^-$  or  $[\text{Th}(\text{NO}_3)_6]^{2-}$ . Spectrophotometric studies indicated that the two kinds of complex can be adsorbed onto the anion exchange resins [23]. The batch experiments at higher acidity confirmed this and the resins reached the best adsorption in 9 M  $\text{HNO}_3$ . Considering the practical application in nuclear fuel cycle process, in the following experiments for the adsorption kinetics and adsorption isotherm, we used 3 M  $\text{HNO}_3$ .

Fig. 4. (Color online) Effect of  $\text{HNO}_3$  concentration on adsorption of 10 mM Th(IV) by the anion exchangers at 298 K in contact time of 2 h.

## 2. Adsorption kinetics

As shown in Fig. 5(a), the adsorption reaches equilibrium quickly, indicating that the resins have notable adsorption kinetics. The pseudo-first order kinetics model of Eq. (1) and pseudo-second order kinetics model of Eq. (2) were adopted to evaluate the mechanism of the adsorption kinetics.

$$q_t = q_e(1 - e^{-k_1 t}), \quad (4)$$

$$q_t = \frac{t q_e^2}{1/k_2^2 + q_e t}, \quad (5)$$

where,  $q_t$  (mg/g) denotes the adsorption quantity at any time before equilibrium;  $q_e$  (mg/g) denotes the equilibrium adsorption quantity; and  $k_1$  and  $k_2$  are constant related to the rate of adsorption.

Figures 5(a) and 5(b) show the fitting curves with pseudo-first order kinetics and pseudo-second order kinetics models. The parameters calculated from the fitting results are listed in Table 2. The correlation coefficients ( $R^2$ ) suggest that pseudo-second order kinetics model fit the adsorption of thorium better, implying that thorium is adsorbed onto the resins in anion forms and the adsorption process is completed as a chemical reaction.

It was found that the adsorption rate of SiPyR-N3 was the smallest of all the three resins. SiPyR-N3 needed about 30 min to attain equilibrium, while SiPyR-N4 and AR-01 took only about 10 minutes. This is due to the fact that pore size of SiPyR-N3 is the smallest of all the three resins. So, enlarging resin pore size promotes the flow and diffusion of thorium anions, leading to faster adsorption rate.

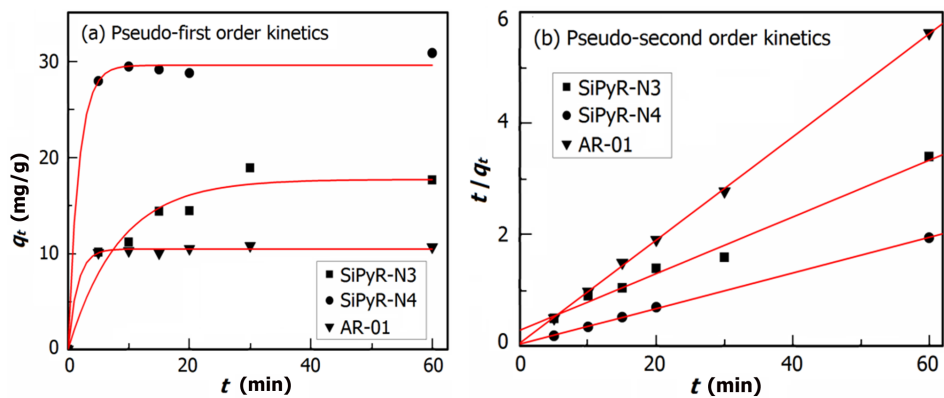


Fig. 5. (Color online) Fitting curves for experimental data of thorium adsorption onto silica-based anion exchange resins with pseudo-first order kinetics model (a) and pseudo-second order kinetics model (b). [HNO<sub>3</sub>]: 3 M; Shaking at 120 r/min; Initial Th content: 10 mM.

TABLE 2. Parameters derived from fitting curves for adsorption kinetics of thorium onto silica-based anion exchange resins

Adsorbent	Pseudo-first order kinetics			Pseudo-second order kinetics		
	$K_1$ (min <sup>-1</sup> )	$Q_e$ (mg/g)	$R^2$	$K_2$ (g/(mg min))	$Q_e$ (mg/g)	$R^2$
SiPyR-N3	0.119	17.704	0.9510	0.0093	19.639	0.9860
SiPyR-N4	0.577	29.602	0.9966	0.0338	31.260	0.9995
AR-01	0.156	10.600	0.9905	0.0564	11.331	0.9993

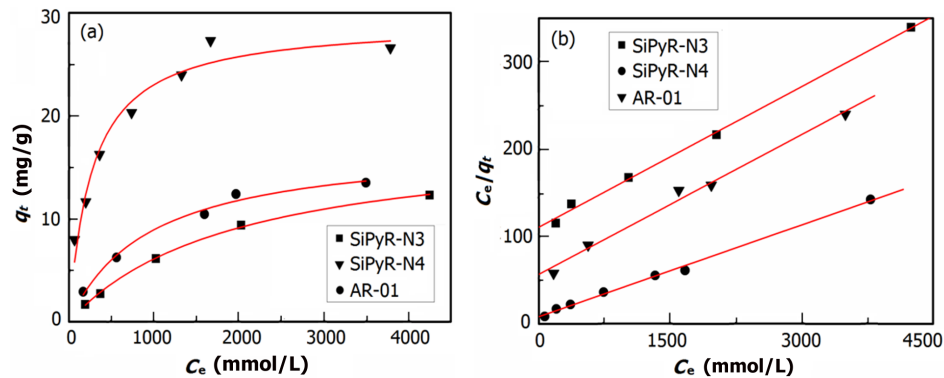


Fig. 6. (Color online) Th adsorption isotherm (a) and isotherm fitting (b) at 298 K. [HNO<sub>3</sub>]: 3 M; Shaking at 120 r/min; Contact time: 2 h.

3. Adsorption isotherm

The results are shown in Fig. 6(a). A theoretical isotherm model, Langmuir equation, was used to calculate the maximum capacity. Assuming that the adsorption process is a monolayer adsorption on a homogeneous surface [24], it is described as follows:

C<sub>e</sub>/Q<sub>e</sub> = C<sub>e</sub>/Q<sub>max</sub> + 1/(K<sub>L</sub>Q<sub>max</sub>), (6)

where C<sub>e</sub> (mmol/L) is the equilibrium concentration of thorium in aqueous phase; Q<sub>e</sub> (mmol/g) and Q<sub>max</sub> (mmol/g) are the adsorption quantity at equilibrium and saturation, respectively; and K<sub>L</sub> (L/mmol) is the Langmuir constant which relates to the energy of adsorption.

Figure 6(b) shows the linear Langmuir adsorption isotherms for the silica-based anion exchange resins. Key pa-

TABLE 3. Parameters derived from the fitting curves of the adsorption isotherm of Th by silica-based anion exchange resins

Adsorbent	$R^2$	$Q_e$ (mg/g)	$Q_m$ (mg/g)
SiPyR-N3	0.997	12.290	18.643
SiPyR-N4	0.996	27.286	28.555
AR-01	0.995	12.401	17.461

rameters derived from the fitting are given in Table 3. The R<sup>2</sup> data indicate that the adsorption of thorium obeys the Langmuir model and the adsorption is supposed to be monolayer adsorption controlled by homogeneous active sites of the resins. From Table 3, thorium adsorption capacity of SiPyR-N4, evaluated at 27–28 mg/g-resin, is the largest of all the three resins.

## 4. Influence of nitrate

Figure 7 shows the adsorption behavior of thorium in 3 M and 6 M HNO<sub>3</sub> solutions, with changing concentrations of NaNO<sub>3</sub>. It was observed that NaNO<sub>3</sub> promotes the adsorption of thorium obviously. Figure 8 shows thorium adsorption in 0.1 M HNO<sub>3</sub> with different concentrations of Mg(NO<sub>3</sub>)<sub>2</sub>. For comparison, the HNO<sub>3</sub> concentration effects in Fig. 4 are presented here in the dotted lines. It can be seen that the distribution coefficient increases with the amount of Mg(NO<sub>3</sub>)<sub>2</sub>, indicating that Mg(NO<sub>3</sub>)<sub>2</sub> promotes the adsorption of thorium effectively. Also, at the same NO<sub>3</sub><sup>-</sup> concentration, the existence of H<sup>+</sup> reduces the thorium retention, being similar to the result in Ref. [23].

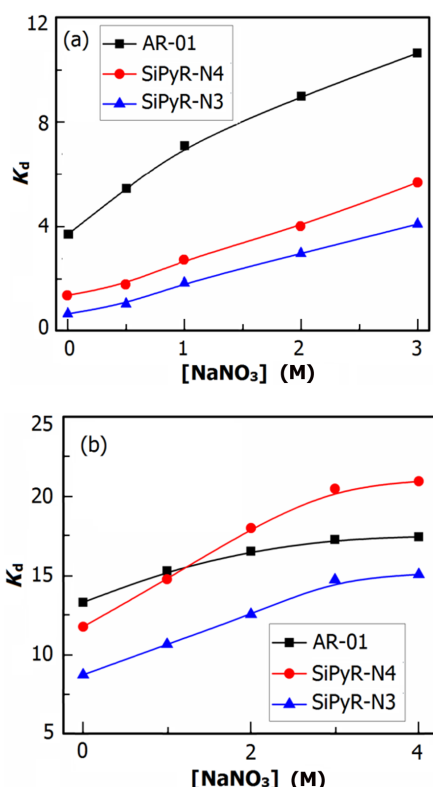
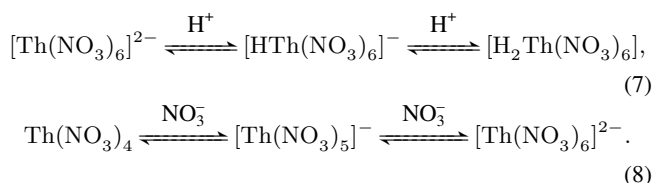


Fig. 7. (Color online) Adsorption of thorium in (a) 3 M HNO<sub>3</sub> – *x* M NaNO<sub>3</sub> (*x* = 0–3) and (b) 6 M HNO<sub>3</sub> – *x* M NaNO<sub>3</sub> (*x* = 0–4); Shaking at 120 r/min; Initial thorium content: 10 mM; Contact time: 2 h.

This phenomenon can be explained with following dynamic equilibrium:



From Eq. (7), increasing the amount of H<sup>+</sup> ions reduces the amount of thorium anions that can be adsorbed by the anion exchange resin in the solution, and accordingly decrease the

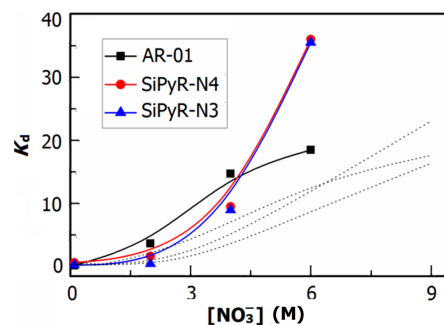


Fig. 8. (Color online) Adsorption of thorium in 0.1 mM HNO<sub>3</sub> at [Mg(NO<sub>3</sub>)<sub>2</sub>] = 0–3 M. Shaking frequency: 120 r/min; Initial Th concentration: 10 mM; Contact time: 2 h; The data in Fig. 4 are presented in the dotted lines for comparison.

adsorption of thorium. In the solution with a constant concentration of H<sup>+</sup>, adding NaNO<sub>3</sub> or Mg(NO<sub>3</sub>)<sub>2</sub> increases the NO<sub>3</sub><sup>-</sup> concentration and therefore increases concentration of thorium anions as described in Eq. (8). As a result, the anion exchange process is promoted. So, NO<sub>3</sub><sup>-</sup> promotes the thorium adsorption and H<sup>+</sup> decreases the thorium retention.

In Section III B 1, thorium is better adsorbed in 9 M HNO<sub>3</sub>. By adding of nitrates, such as NaNO<sub>3</sub> or Mg(NO<sub>3</sub>)<sub>2</sub>, it is feasible to achieve a better adsorption of thorium at a relatively low acidity, 3–6 M for example.

## 5. Adsorption thermodynamics

The values of standard  $\Delta H^0$  and  $\Delta S^0$  for thorium in the anion exchange reactions were calculated from the slopes and intercepts of the linear Van't Hoff equation as shown in Eq. (9). The results are shown in Fig. 9.

$$\ln K_d = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (9)$$

The Gibbs free energy of the adsorption,  $\Delta G^0$  can be calculated by Eq. (10):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0, \quad (10)$$

where,  $R$  is the gas constant (8.314 J/(mol K)),  $K_d$  is the distribution coefficient and  $T$  is temperature (K).

The thermodynamic parameters are given in Table 4. The negative  $\Delta G$  values indicate that the adsorption processes took place spontaneously. The enthalpy change values are negative, which indicates that the adsorption of thorium is an exothermic process.

## 6. Adsorption of thorium from accompany metal ions in nitric acid solution

As shown in Fig. 10, of all the eight metal ions, palladium has the strongest affinity to the anion exchange resins, which agree with the result in Ref. [13]. So, the existence of palladium is quiet adverse to the thorium adsorption. So, we

TABLE 4. Thermodynamic parameters of thorium adsorption onto the resins

	SiPyR-N3		SiPyR-N4		AR-01	
$\Delta H$ (kJ/mol)	-2.88		-2.47		-2.79	
$\Delta S$ (J/(mol K))	12.78		17.7		15.33	
T (K)	$\Delta G$ (kJ/mol)	$T\Delta S$ (kJ/mol)	$\Delta G$ (kJ/mol)	$T\Delta S$ (kJ/mol)	$\Delta G$ (kJ/mol)	$T\Delta S$ (kJ/mol)
298.15	-6.69	3.81	-7.75	5.28	-7.36	4.57
303.15	-6.75	3.87	-7.84	5.37	-7.44	4.65
308.15	-6.82	3.94	-7.92	5.45	-7.51	4.72
313.15	-6.88	4.00	-8.01	5.54	-7.59	4.80
318.15	-6.95	4.07	-8.10	5.63	-7.67	4.88

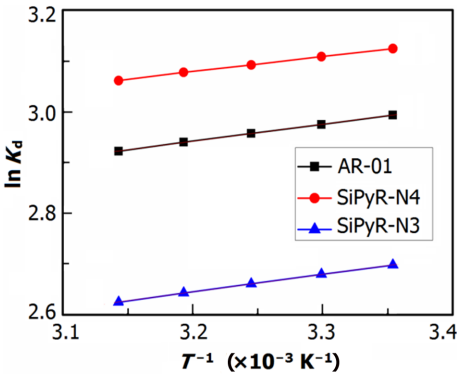


Fig. 9. (Color online) LLS plots for thermodynamic parameters. Shaking: 120 r/min; Initial Th content: 10 mM; Contact time: 2 h;  $[\text{HNO}_3]$ : 9 M.

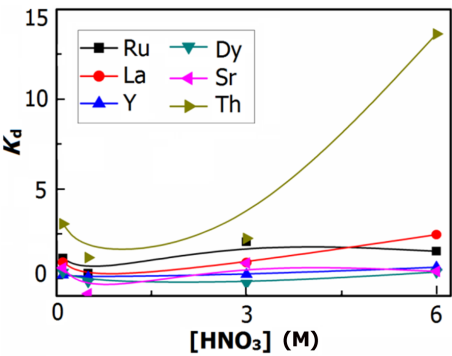


Fig. 11. (Color online) Adsorption of thorium and the accompanying metal ions (without Pd); Shaking frequency: 120 r/min; Initial concentration of metals: 10 mM; Contact time: 2 h.

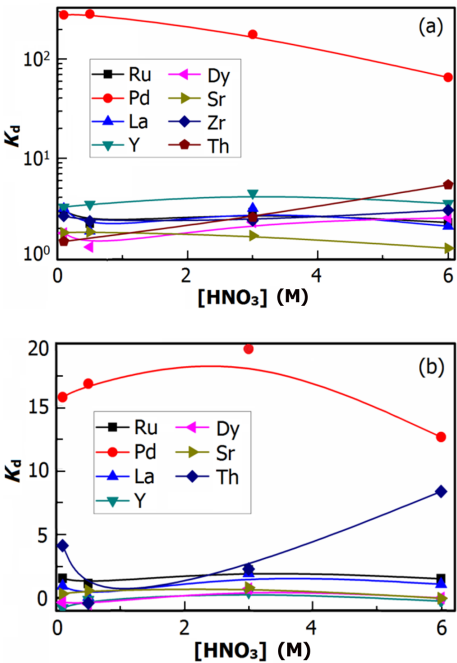


Fig. 10. (Color online) Adsorption of thorium and the accompanying metal ions on anion exchange resins of (a) SiPyR-N3 and (b) SiPyR-N4. Shaking frequency: 120 r/min; Initial concentration of metals: 10 mM; Contact time: 2 h.

should remove palladium from the solutions with SiPyR-N3 and then find a method to separate thorium from the other metal ions.

Figure 11 shows the thorium adsorption under accompanying metal ions except palladium using SiPyR-N4. It can be seen that the resin shows a stronger adsorption of thorium than other metal ions at high  $\text{HNO}_3$  concentration. The adsorption onto AR-01 is similar to SiPyR-N4. This means that thorium can be separated from accompanying metals at high concentration of nitric acid, 6–9 M for example.

Therefore, it is feasible to separate thorium from the accompanying metal ions in  $\text{HNO}_3$  solutions by removing palladium with SiPyR-N3 before, recovering thorium from accompanying metal ions with SiPyR-N4 or AR-01.

### C. Desorption experiment

The eluent was 0.1 M nitric acid. After only 5 min, almost all the thorium adsorbed onto the resins could be eluted and the recovery was almost 100%. The elution of thorium was quite easy, as reported in literatures [22].

## IV. CONCLUSION

Three kinds of macro-porous silica-based anion exchange resins were synthesized, and applied for the first time in ad-

sorption of thorium in nitric acid solutions. The following conclusions can be drawn from the experimental investigation of the thorium adsorption:

- (1) The adsorption procedure is of monolayer adsorption on a homogeneous surface, obeying the pseudo-second order kinetic equation;
- (2) Of all the three resins, SiPyR-N4 exhibits the best kinetics and greatest adsorption capacity;
- (3) At higher concentration of nitric acid, thorium has shown a better affinity to the resins;
- (4)  $\text{NO}_3^-$  can promote the adsorption of thorium and  $\text{H}^+$  can decrease the retention of thorium obviously;
- (5) Adsorption of thorium is an exothermic reaction;

(6) By using SiPyR-N3 and SiPyR-N4, thorium can be separated from the accompanying metals; and

(7) The adsorbed thorium could be eluted with 0.1 M nitric acid solution easily.

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